

Communication

Three novel bismetallacyclopropa[60]fullerene complexes formed via intermediate monometallacyclopropa[60]fullerene diphosphine ligands

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Received 6 October 2004; accepted 9 December 2004

Available online 7 February 2005

Abstract

The homodinuclear bismetallacyclopropa[60]fullerene complexes ($\eta^2\text{-C}_{60}$)M($\mu\text{-}\eta^1, \eta^1\text{-trans-Ph}_2\text{PCH=CH PPh}_2$)₂M($\eta^2\text{-C}_{60}$) (**1**, M = Pt; **2**, M = Pd) were prepared by reaction of C₆₀ with M(dba)₂ (dba = dibenzylideneacetone) and *trans*-1,1'-bis(diphenylphosphino)ethylene in 82% and 92% yield, whereas reaction of C₆₀ with Pd(dba)₂ and *trans*-dppet followed by treatment with C₆₀ and Pt₂(dba)₃ gave rise to the heterodinuclear complex ($\eta^2\text{-C}_{60}$)Pd($\mu\text{-}\eta^1, \eta^1\text{-trans-Ph}_2\text{PCH=CH PPh}_2$)₂Pt($\eta^2\text{-C}_{60}$) (**3**) in 65% yield. Mechanistic study showed that these reactions involve the intermediates of monometallacyclopropa[60]fullerene diphosphine ligands ($\eta^2\text{-C}_{60}$)M($\eta^1\text{-trans-Ph}_2\text{PCH=CHPPh}_2$)₂ (**4**, M = Pt; **5**, M = Pd). All the mono- and bismetallacyclopropa[60]fullerene complexes **1–5** have been fully characterized by elemental analysis and spectroscopy, as well as for **2** by X-ray crystallography. © 2004 Elsevier B.V. All rights reserved.

Keywords: Palladium; Platinum; [60]fullerene; Bis(diphenylphosphino)ethylene; X-ray structure

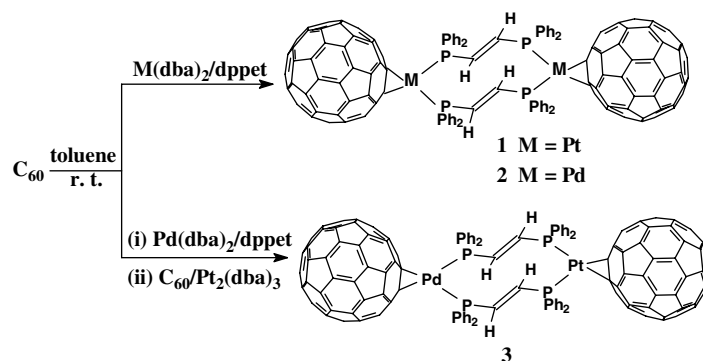
Metallacyclopropa[60]fullerenes have received considerable attention, since metal coordination may have great effects on the chemical and physical properties of [60]fullerene [1]. Among such fullerene derivatives bis- and multimetallacyclopropa[60]fullerenes are of particular interest; this is largely because new chemical and physical properties might be possibly induced through interactions between C₆₀ spheres and/or metal centers [2,3]. On the basis of our study on metallacyclopropa[60]fullerenes [4], we have recently synthesized and characterized three novel bismetallacyclopropa[60]fullerenes ($\eta^2\text{-C}_{60}$)M($\mu\text{-}\eta^1, \eta^1\text{-trans-Ph}_2\text{PCH=CH PPh}_2$)₂M($\eta^2\text{-C}_{60}$) (**1**, M = Pt; **2**, M = Pd) and ($\eta^2\text{-C}_{60}$)Pd($\mu\text{-}\eta^1, \eta^1\text{-trans-Ph}_2\text{PCH=CHPPh}_2$)₂Pt($\eta^2\text{-C}_{60}$) (**3**), in which a ten-membered phosphametallacycle containing

Pt/Pt, Pd/Pd, or Pd/Pt metal centers is sandwiched in between two C₆₀ spheres (Scheme 1).

The preparations of **1** and **2** are as follows. To a stirred purple solution of 72 mg (0.1 mmol) of C₆₀ in 50 ml of toluene were added 66 mg (0.1 mmol) of Pt(dba)₂ (dba = dibenzylideneacetone) and 78 mg (0.2 mmol) of *trans*-dppet (dppet = 1,1'-bis(diphenylphosphino)ethylene) or 114 mg (0.2 mmol) of Pd(dba)₂ and 39 mg (0.1 mmol) of *trans*-dppet. The mixture was stirred for 5 h at room temperature to give a green precipitate. The precipitate was washed successively with toluene, hexane and diethyl ether, and finally dried in vacuum to afford the homodinuclear bisfullerene complexes ($\eta^2\text{-C}_{60}$)Pt($\mu\text{-}\eta^1, \eta^1\text{-trans-Ph}_2\text{PCH=CHPPh}_2$)₂Pt($\eta^2\text{-C}_{60}$) (**1**) and ($\eta^2\text{-C}_{60}$)Pd($\mu\text{-}\eta^1, \eta^1\text{-trans-Ph}_2\text{PCH=CHPPh}_2$)₂Pd($\eta^2\text{-C}_{60}$) (**2**) in 82% and 92% yield. Similarly, the novel heterodinuclear Pd/Pt bisfullerene complex ($\eta^2\text{-C}_{60}$)Pd($\mu\text{-}\eta^1, \eta^1\text{-trans-Ph}_2\text{PCH=CHPPh}_2$)₂Pt($\eta^2\text{-C}_{60}$) (**3**) was prepared as described below. A mixture

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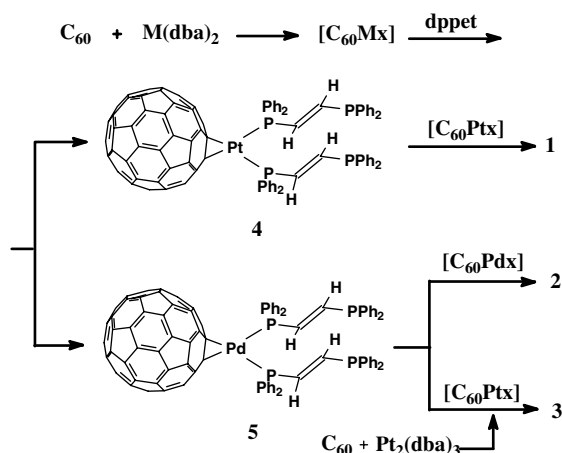


Scheme 1.

consisting of 36 mg (0.05 mmol) of C_{60} , 29 mg (0.05 mmol) of $\text{Pd}(\text{dba})_2$ and 39 mg (0.10 mmol) of *trans*-dppet in 25 ml of toluene was stirred at room temperature for 1 h and then to the resulting green solution were added 36 mg (0.05 mmol) of C_{60} and 28 mg (0.025 mmol) of $\text{Pt}_2(\text{dba})_3$. The new mixture was stirred at this temperature for 5 h to give a precipitate. The same workup as that for **1** and **2** gave 85 mg (65%) of **3**.

Now, the question is how these bismetallacyclopropa[60]fullerene complexes **1–3** could be produced from the “one-pot” reactions described above. To answer this question, we carried out some experiments. From the experiments (see [Supplementary material](#)) it was found that: (i) a toluene solution of C_{60} reacted with $M(\text{dba})_2$ ($M = \text{Pt}, \text{Pd}$) and *trans*-dppet in 1:1:2 molar ratio at room temperature for 1 h to give novel metallacyclopropa[60]fullerene diphosphines ($\eta^2\text{-C}_{60}\text{M}(\eta^1\text{-trans-Ph}_2\text{PCH=CHPPh}_2)_2$ (**4**, $M = \text{Pt}$; **5**, $M = \text{Pd}$) in 35% and 75% yield, respectively; (ii) the isolated **4** in toluene reacted with C_{60} and $\text{Pt}(\text{dba})_2$ in 1:1:1 molar ratio at room temperature for 5 h to give homodinuclear bisfullerene **1** in 59% yield, whereas reaction of the isolated **5** with C_{60} and $\text{Pd}(\text{dba})_2$ afforded homodinuclear bisfullerene **2** in 53% yield; and (iii) reaction of **5** with $[\text{C}_{60}\text{Pt}_x]$ formed in situ from C_{60} and $\text{Pt}_2(\text{dba})_3$ under similar conditions afforded heterodinuclear bisfullerene **3** in 55% yield. On the basis of these observations we can propose a possible pathway (Scheme 2) to answer the above-mentioned question. That is, bismetallacyclopropa[60]fullerenes **1–3** could be produced first by η^1 -coordination of organic diphosphine *trans*-dppet with polymeric species $[\text{C}_{60}\text{M}_x]$ ($M = \text{Pt}, \text{Pd}$; $x \approx 1$) to give metallacyclopropa[60]fullerene diphosphines **4** and **5**, and then by subsequent chelation of **4** as a bidentate ligand with $[\text{C}_{60}\text{Pt}_x]$ and by chelation of **5** with $[\text{C}_{60}\text{Pd}_x]$ or $[\text{C}_{60}\text{Pt}_x]$. The polymeric species $[\text{C}_{60}\text{Pd}_x]$ [**5**] and $[\text{C}_{60}\text{Pt}_x]$ [**6**] were formed apparently from reactions of C_{60} with $\text{Pd}(\text{dba})_2$ and $\text{Pt}(\text{dba})_2$, respectively.

Fullerene complexes **1–5** have been fully characterized by elemental analysis and spectroscopy [7], as well as for bismetallacyclopropa[60]fullerene **2** by X-ray dif-



Scheme 2.

fraction techniques [8]. For instance, the IR spectra of **1–5** displayed four absorption bands in the range 1434–513 cm^{-1} for their C_{60} spheres [9]. In addition, the ^{31}P NMR spectra of **1–3** showed one singlet and one triplet at ca. 20 ppm for their four identical coordinated P atoms, whereas **4** and **5** exhibited two singlets at ca. 20 ppm and ca. –7 ppm for their two identical coordinated P atoms and two identical uncoordinated free P atoms, respectively. That the chemical shifts of the coordinated P atoms lie at much lower field compared to the corresponding free P atoms is due to transfer of the lone pair of electrons from P atom to metal center, which has been well observed for the other phosphine-coordinated fullerene complexes such as $(\eta^2\text{-C}_{60})\text{Pt}(\text{PPh}_3)_2$ [10], $(\eta^2\text{-C}_{60})\text{M}(\text{CO})_3(\text{dppb})$ ($M = \text{Mo}, \text{W}$) [11] and $(\eta^2\text{-C}_{60})\text{M}(\text{CO})_3(\text{DIOP})$ ($M = \text{Mo}, \text{W}$) [12]. The X-ray diffraction analysis revealed that complex **2** (Fig. 1) consists of two C_{60} spheres, which are bridged by two metal centers of a ten-membered metallacycle; the metallacycle is composed of two *trans*-dppet ligands coordinated to Pd/Pd metal centers. Interestingly, **2** is, to our knowledge, the first structurally characterized group 10 metal-containing bismetallacyclopropa [60]fullerenes. The fullerene center-to-center separation of 16.869 Å in Pd_2

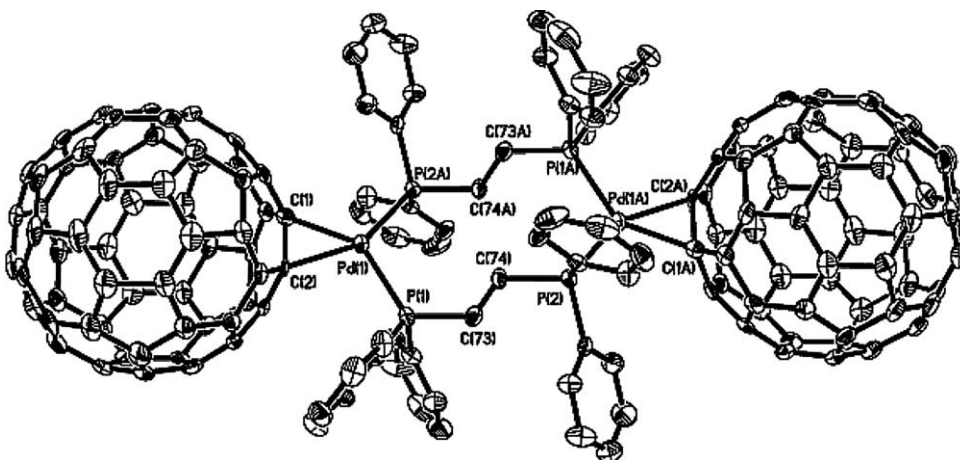


Fig. 1. ORTEP drawing of **2** (30% thermal ellipsoids). Selected bond distances (Å) and angles (°): Pd(1)–C(1) 2.137(11), Pd(1)–C(2) 2.130(9), Pd(1)–P(1) 2.326(3), Pd(1)–P(2A) 2.323(3), C(1)–C(2) 1.473(14) and C(1)–Pd(1)–C(2) 40.4(4), C(1)–Pd(1)–P(1) 141.9(3), P(2A)–Pd(1)–P(1) 109.06(10), P(2A)–Pd(1)–C(1) 107.4(3).

complex **2** is close to that of 16.57 Å in metallacyclopropa[60]fullerene Ir₂ complex, but the non-bonded metal-to-metal distance of 6.83 Å for **2** is much shorter than the corresponding intermetallic distance of 8.104 Å in the Ir₂ complex [13]. The two C–C double bonds C(73)–C(74)=C(73A)–C(74A) = 1.290(14) Å for **2** are slightly shorter than the common C–C double bond (1.34 Å). Each of the zero-valent Pd(0) centers has a square-planar geometry. The η²-coordinated 6:6 bonds, for example, C(1)–C(2) = 1.473(14) Å is obviously longer than the other 58 uncoordinated 6:6 bonds in each C₆₀ sphere due to the metal-to-C₆₀ π-back donation [1a].

In conclusion, we have synthesized three novel bismetallacyclopropa[60]fullerene complexes **1–3**, in which a 10-membered metallacycle is sandwiched in between two C₆₀ moieties. A mechanistic study on the “one-pot” reactions leading to complexes **1–3** has allowed us to obtain two novel metallacyclopropa[60]fullerene diphosphines **4** and **5** in high yield. In view of the widespread uses of phosphorus-containing ligands in transition metal chemistry, these two metallacyclopropa[60]fullerene diphosphines **4** and **5** would play an important role in the development of transition metal fullerene chemistry. Further applications of diphosphines **4** and **5** in preparation of other bismetallacyclopropa[60]fullerene complexes are under intensive studies.

Acknowledgements

We are grateful to the National Natural Science Foundation of China and the Research Fund for the Doctoral Program of Higher Education of China for financial support.

Appendix A. Supplementary data

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 232273 for compound **2**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: <http://www.deposit@ccdc.cam.ac.uk> or <http://www.ccdc.cam.ac.uk>). A text describing the detailed synthesis and characterization of **1–5** may be obtained on request. Supplementary data associated with this article can be found, in the online version at [doi:10.1016/j.jorganchem.2004.12.006](https://doi.org/10.1016/j.jorganchem.2004.12.006).

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- [7] **1**: m.p. >300 °C. ^1H NMR (300 MHz, $\text{CS}_2/\text{CDCl}_3$): δ 6.90–7.60 (m, 44 H, $8\text{C}_6\text{H}_5$, 4=CH). ^{31}P NMR (121.48 MHz, $\text{CS}_2/\text{CDCl}_3$): δ 19.71 (t, $J_{\text{Pt-P}} = 3794$ Hz, 4P). IR (KBr): ν_{C60} 1434s, 1183m, 577m, 524vs; $\nu_{\text{C=C}}$ 1571m, 969m cm^{-1} . Anal. Found: C, 78.71; H, 1.70. Calc. for $\text{C}_{172}\text{H}_{44}\text{P}_4\text{Pt}_2$: C, 78.72; H, 1.69%. **2**: m.p. >300 °C. ^1H NMR (300 MHz, $\text{CS}_2/\text{CDCl}_3$): δ 7.20–7.66 (m, 44H, $8\text{C}_6\text{H}_5$, 4=CH); ^{31}P NMR (121.48 MHz, $\text{CS}_2/\text{CDCl}_3$): δ 20.22 (s, 4 P). IR (KBr): ν_{C60} 1432m, 1183m, 577m, 524vs; $\nu_{\text{C=C}}$ 1571m, 964m cm^{-1} . Anal. Found: C, 84.16; H, 2.00. Calc. for $\text{C}_{172}\text{H}_{44}\text{P}_4\text{Pd}_2$: C, 84.43; H, 1.81%. **3**: m.p. >300 °C. ^1H NMR (300 MHz, $\text{CS}_2/\text{CDCl}_3$): 7.08–7.60 (m, 40H, C_6H_5 ; 4H, =CH); ^{31}P NMR (121.48 MHz, $\text{CS}_2/\text{CDCl}_3$): 19.79 (s, 2P, PdP), 20.12 (t, 2P, $J_{\text{Pt-P}} = 3848$ Hz, PtP) ppm; IR (KBr): $\nu_{\text{C=C}}$ 1571(m), 967(m); ν_{C60} 1434(s), 1183(m), 579(m), 523(vs) cm^{-1} . Anal. Found: C, 81.40; H, 2.00. Calc. for $\text{C}_{172}\text{H}_{44}\text{P}_4\text{PdPt}$: C, 81.47; H 1.75%. **4**: m.p. >300 °C. ^1H NMR (300 MHz, $\text{CS}_2/\text{CDCl}_3$): δ 7.24–7.60 (m, 44H, $8\text{C}_6\text{H}_5$, 4=CH); ^{31}P NMR (121.48 MHz, $\text{CS}_2/\text{CDCl}_3$): δ 19.88 (t, $J_{\text{Pt-P}} = 3682$ Hz, 2P, 2PtP), –7.24 (s, 2P, 2Ph₂P). IR (KBr): ν_{C60} 1434s, 1184m, 577m, 524vs; $\nu_{\text{C=C}}$ 1571m, 967m cm^{-1} . Anal. Found: C, 78.75; H, 2.41. Calc. for $\text{C}_{112}\text{H}_{44}\text{P}_4\text{Pt}$: C, 78.73; H, 2.60%. **5**: m.p. >300 °C. ^1H NMR (300 MHz, $\text{CS}_2/\text{CDCl}_3$): δ 7.09–7.63 (m, 44H, $8\text{C}_6\text{H}_5$, 4=CH); ^{31}P NMR (121.48 MHz, $\text{CS}_2/\text{CDCl}_3$): δ 20.21 (s, 2P, 2PdP), –7.48 (s, 2P, 2Ph₂P). IR (KBr): ν_{C60} 1434s, 1183m, 578m, 513vs; $\nu_{\text{C=C}}$ 1570m, 966m cm^{-1} . Anal. Found: C, 82.87; H, 2.75. Calc. for $\text{C}_{112}\text{H}_{44}\text{P}_4\text{Pd}$: C, 83.04; H, 2.74%.
- [8] X-ray data for **2**: $\text{C}_{172}\text{H}_{44}\text{P}_4\text{Pd}_2$, Monoclinic, $P2(1)/c$, $a = 13.9731(13)$, $b = 13.6933(13)$, $c = 34.671(3)$ Å, $\beta = 109.149(5)^\circ$, $V = 6266.8(10)$ Å³, $Z = 2$, $D_c = 1.510$ g/cm³, $F(000) = 2874$, $T = 293$ K., GOF = 1.082. The structure was solved by direct methods using Bruker SMART 1000 automated diffractometer equipped with a graphite monochromator with Mo K α radiation ($\lambda = 0.71073$ Å). All nonhydrogen atoms were refined using anisotropic thermal parameters. A total of 18461 independent reflections were collected, of which 8160 reflections with $I > 2\sigma(I)$ were considered to be observed and used to structural refinements. Data were corrected for Lp and absorption. Final $R = 0.0803$ and $R_w = 0.1855$. The largest peak in final difference map was 0.886 e Å⁻³.
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